EFFECT OF CARBON DIOXIDE (CO_2) SUPPRESSION ON EXPLOSIVE LIMITS OF METHANE

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ABSTRACT

Knowledge of the explosion hazards of gaseous fuels is of importance to ensure the safety in industrial and domestic applications that produce or use flammable mixtures. Thus, the experiment is conducted to determine the upper and lower flammability limits of methane based on volume percent of inert gas (CO_2). The purpose of the experiment to reduce the concentration of oxygen below the limiting oxygen concentration (LOC) for the purpose of lowering the likelihood of explosion. The inert gas is usually nitrogen or carbon dioxide, although sometimes steam may be used. But in this experiment, gas CO_2 was used. The experiments were performed in a 20 L closed explosion vessel. The mixtures were ignited by using spark permanent wire that placed at the centre of the vessel. In this study, the result shows the lower explosive limit (LEL) and upper explosive limit (UEL) for CH_4 start from 5 vol % to 19 vol % and have revealed that the addition of suppression agent as 5 vol % and 10 vol % of CO_2 in CH_4 extends the LEL and UEL initially 6 vol % to 12 vol % and 3 vol % to 6 vol %.

ABSTRAK

Pengetahuan tentang bahaya letupan bahan api gas adalah penting untuk menjamin keselamatan dalam industri dan aplikasi dalam negeri yang menghasilkan atau menggunakan campuran mudah terbakar. Dengan demikian, percubaan dilakukan untuk menentukan batas atas dan bawah dari metana mudah terbakar berdasarkan peratus kelantangan gas inert (CO_2). Tujuan percubaan untuk mengurangkan kepekatan oksigen di bawah kepekatan oksigen menyekat (LOC) untuk tujuan menurunkan kemungkinan letupan. Gas inert ini biasanya nitrogen atau karbon dioksida, walaupun kadang-kadang stim boleh digunakan. Namun dalam percubaan ini, gas karbon dioksida (CO_2) digunakan. Percubaan dilakukan dalam 20-L tertutup kapal letupan. Campuran yang dinyalakan dengan menggunakan percikan kawat kekal yang ditempatkan di tengah-tengah kapal. Dalam kajian ini, hasilnya menunjukkan batas letupan rendah (LEL) dan batas letupan atas (UEL) untuk CH_4 adalah dari 5 % vol hingga 19 % vol dan telah mendedahkan bahawa penambahan agen penindasan sebagai 5 % vol dan 10 % vol CO_2 di CH_4 memperluaskan LEL dan UEL awalnya 6 % vol hingga 12 % vol dan 3 % vol ke 6 % vol.

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LIST OF ABBREVIATIONS

CH4	- Methane
CO2	- Carbon Dioxide
Vol %	- Volume Percent
LEL	– Lower Explosion Limits
UEL	– Upper Explosion Limits
P max	– Maximum Pressure
dp/dt	– Maximum Rate of Explosion Pressure Rise
Kg	– Gas Vapor Deflagration Index

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Knowledge of the explosion hazards of gaseous fuels is of importance to ensure the safety in industrial and domestic applications that produce or use flammable mixtures. In accordance with generally accepted usage, the flammability limits are known as those regions of fuel–air ratio within which flame propagation can be possible and beyond which flame cannot propagate. And there are two distinct separate flammability limits for the fuel–air mixture, namely, the leanest fuel-limit up to which the flame can propagate is termed as lower flammability limit (LFL), and the richest limit is called as upper flammability limit (UFL).

It is now acknowledged that flammability limits are physical–chemical parameters of flammable gases and vapors of flammable liquids, which are related to many factors including the heat losses from the flame by conduction, convection and radiation to the apparatus walls, instabilities in the flame front resulting from buoyant convection, selective diffusion and flame stretch, as well as radical loss or their generation on apparatus walls. Thus, more attentions have been given to the study the effects of environmental parameters, such as the vessel size, initial temperature and pressure, on this fundamental characteristic. The standardized measurements of flammability limits are usually conducted in the flammability tubes or closed vessels.

Generally, large size of combustion charmer can minimize the wall effects and potentially allow to the use of strong igniters to ensure the absence of ignition limitation, so most of the flammability measurements were conducted in the closed chambers recently. In combustion vessel test, spark igniter is commonly adopted. It is known that the minimum ignition energy is a strong function of the compositions near the flammability limits.

There are several criteria to determine the flammability limits in experimental measurements. A successful attempt can be determined by one or a combination of the following two criteria: (1) visualization inspection of the flame kernel development produced by the spark, namely visual criterion; (2) measurements of the pressure and/or temperature histories in the vessel, where an appropriate pressure or temperature rise criteria can be used to designate flammability rather than the purely visual observation of flame generation.

There exist large array of experimental data on flammability limits for gaseous mixtures of fuel–air–inerts, and the inerts gases considered herein were nitrogen gas, carbon dioxide or their mixture, which are to different from the real residual gaseous in combustion chamber, and most of previous studies were conducted at atmospherical conditions. For engineering application, the fundamental research on flammability characteristics of fuel–air mixtures with combustion bomb meter, especially at high temperature and pressure like those of combustion is worthwhile. Practically, due to the time consumed in measurements, it is desirable to choose some reliable criteria for quick estimation of flammability limits.

1.2 Scope of study

Thus, for the purpose of prediction of effect CO_2 of flammability limits in CH_4/air structure, this is the contents of the scope of study:

For this experiment, equipment that can be used is a bomb explosion unit. This unit usually has five streams which one will indicate the air/oxygen (O_2) and the other stream are fuel and inert stream.

This experiment is conducted to determine the upper and lower flammability limit of CH_4 based on volume percent of inert gas (CO_2).

A type of fuel hydrocarbon that is selected to be examined out is CH_4 and mixed with CO_2. For the air stream, normally source of air is directly taken from the surroundings.

1.3 Objectives Research

To predict the upper/lower explosive limit of a mixture composed of hydrocarbon and inert CO_2. Different methods have been proposed to predict the explosive limits, especially the lower explosive limit (LEL), for pure flammable gases.

To determine the effect of CO_2 suppressing on flammability limits of premixed CH_4-air mixture in a combustion bomb at atmospheric pressure and ambient temperature.

To reduce the concentration of oxygen below the limiting oxygen concentration (LOC) for the purpose of lowering the likelihood of explosion. The inert gas is usually N_2 or CO_2, although sometimes steam may be used. But in this experiment, CO_2 was used.

1.4 Problem Statement

An early detection of an explosion is very important especially in the process industries as a prevention and explosion protection. A disadvantage this method is potential of the suppression agent to mitigate the explosion limits especially when dealing with CH_4 as a fuel source. This problem can be solved by added different vol % of suppression agent, CO_2 with the one which are more effectives and can be rely on.

CHAPTER 2

LITERATURE RIVIEW

2.1 Carbon Dioxide (CO_2)

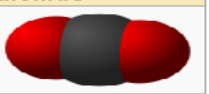
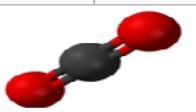
Carbon dioxide (chemical formula CO_2) is a chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. It is a gas at standard temperature and pressure and exists in earth's atmosphere in this state. CO_2 is a trace gas being only 0.038 % of the atmosphere.

Carbon dioxide is used by plants during photosynthesis to make sugars, which may either be consumed in respiration or used as the raw material to produce other organic compounds needed for plant growth and development. It is produced during respiration by plants, and by all animals, fungi and microorganisms that depend either directly or indirectly on plants for food. It is thus a major component of the carbon cycle. Carbon dioxide is generated as a by-product of the combustion of fossil fuels or the burning of vegetable matter, among other chemical processes. Small amounts of carbon dioxide are emitted from volcanoes and other geothermal processes such as hot springs and geysers and by the dissolution of carbonates in crustal rocks.

Carbon dioxide has no liquid state at pressures below 5.1 atmospheres. At 1 atmosphere (near mean sea level pressure), the gas deposits directly to a solid at temperatures below −78 °C (−108.4 °F; 195.1 ^{o}K) and the solid sublimes directly to a gas above −78 °C. In its solid state, carbon dioxide is commonly called dry ice.

Carbon dioxide is used in enhancing oil recovery where it is injected into or adjacent to producing oil wells, usually under supercritical conditions. It acts as both a pressurizing agent and, when dissolved into the underground crude oil, significantly reduces its viscosity, enabling the oil to flow more rapidly through the earth to the removal well. In mature oil fields, extensive pipe networks are used to carry the carbon dioxide to the injection points.

Table 2.1: Properties of Carbon Dioxide (CO_2)

Carbon dioxide	
O=C=O 116.3 pm	
	
Properties	
Molecular formula	CO_2
Molar mass	44.010 g/mol
Appearance	colorless, odorless gas
Density	1.562 g/mL (solid at 1 atm and −78.5 °C) 0.770 g/mL (liquid at 56 atm and 20 °C) 1.977 g/L (gas at 1 atm and 0 °C) 849.6 g/L (supercritical fluid at 150 atm and 30 °C
Melting point	-78 °C, 194.7 K, -109 °F (*subl.*)
Boiling point	-57 °C, 216.6 K, -70 °F (at 5.185 bar)
Solubility in water	1.45 g/L at 25 °C, 100 kPa
Acidity (pK_a)	6.35, 10.33
Refractive index (n_D)	1.1120
Viscosity	0.07 cP at −78 °C
Dipole moment	zero

2.2 Methane (CH_4)

Methane is a chemical compound with the chemical formula CH_4. It is the simplest alkane, and the principal component of natural gas. Methane's bond angles are 109.5 ^oC. Burning methane in the sufficient presence of oxygen produces carbon dioxide and water. The relative abundance of methane makes it an attractive fuel. However, because it is a gas at normal temperature and pressure, methane is difficult to transport from its source. In its natural gas form, it is generally transported in bulk by pipeline or LNG carriers; few countries transport it by truck.

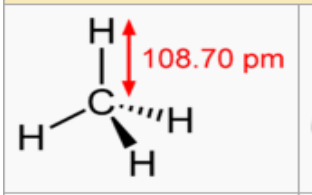
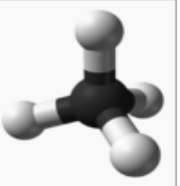
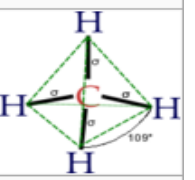
Methane is a relatively potent greenhouse gas with a high global warming potential of 72 (averaged over 20 years) or 25 (averaged over 100 years). Methane in the atmosphere is eventually oxidized, producing carbon dioxide and water. As a result, methane in the atmosphere has a half life of seven years.

Methane can trap about 20 times the heat of CO_2. In the same time period, CO_2 increased from 278 to 365 parts per million. The radiative forcing effect due to this increase in methane abundance is about one-third of that of the CO_2 increase. In addition, there is a large, but unknown, amount of methane in methane clathrates in the ocean floors. The earth's crust contains huge amounts of methane. Large amounts of methane are produced anaerobically by methanogenesis. Other sources include mud volcanoes, which are connected with deep geological faults, landfill and livestock (primarily ruminants) from enteric fermentation.

Methane is used in industrial chemical processes and may be transported as a refrigerated liquid (liquefied natural gas, or LNG). While leaks from a refrigerated liquid container are initially heavier than air due to the increased density of the cold gas, the gas at ambient temperature is lighter than air. Gas pipelines distribute large amounts of natural gas, of which methane is the principal component.

In the chemical industry, methane is the feedstock of choice for the production of hydrogen, methanol, acetic acid, and acetic anhydride. When used to produce any of these chemicals, methane is first converted to synthesis gas, a mixture of carbon monoxide and hydrogen, by steam reforming. In this process, methane and steam react on a nickel catalyst at high temperatures (700–1100 °C).

Table 2.2: Properties of Methane (CH_4)

Methane	
	
	
other names [hide] Methyl hydride, Marsh gas, firedamp	
Identifiers	
CAS number	74-82-8 ✓
PubChem	297
ChemSpider	291
SMILES	[show]
InChI	[show]
Properties	
Molecular formula	CH_4
Molar mass	16.042 g/mol
Appearance	Colorless gas
Density	0.717 kg/m^3 (gas, 0 °C) 415 kg/m^3 (liquid)
Melting point	-182.5 °C, 91 K, -297 °F
Boiling point	-161.6 °C, 112 K, -259 °F
Solubility in water	35 mg/L (17 °C)

2.3 20-Liter Spherical Explosion Vessel

The experimental 20-L-Apparatus (or 20 Liter Spherical Explosion Vessel) was obtained from Adolf Kühner AG. The test chamber is a stainless steel hollow sphere with a personal computer interface. The top of the cover contains holes for the lead wires to the ignition system. The opening provides for ignition by a condenser discharging with an auxiliary spark gap (Siwek, 1996; Operating Instructions for the 20-L-Apparatus, 1996), which is controlled by the KSEP 310 unit of the 20-L-Apparatus. The KSEP 332 unit uses piezoelectric pressure sensors to measure the pressure as function of time (ASTM, 1991; Operating Instructions for the 20-L-Apparatus, 1996). A comprehensive software package KSEP 5.0 is available, which allows safe operation of the test equipment and an optimum evaluation of the explosion test results.

In recent years, international standard use has been made of the more convenient and less expensive 20-L-Apparatus as the standard equipment. The explosion behavior of combustible materials (combustible dusts, flammable gases, or solvent vapors) must be investigated in accordance with internationally recognized test procedures. For the determination of combustible gases or vapors, the test is generally accomplished in a quiescent state (ignition delay time, $t_v = 0$ sec) (Operating Instructions for the 20-L-Apparatus, 1996).

In the 20-L-Apparatus, important explosion characteristics of gases and vapors, such as flammability limits, maximum explosion overpressure (Pmax), gas or vapor deflagration index (Kg), and minimum oxygen concentration (MOC), can be determined with adherence to standardized test procedures.

2.4 Maximum Explosion Overpressure (Pmax), Maximum Rate of Explosion Pressure Rise (dP/dt)max, and Gas or Vapor Deflagration Index (Kg)

The peak values that accompany the explosion of a combustible vapor are the maximum pressure (Pmax) and the maximum rate of explosion pressure rise (dP/dt)max. Experimentally, the peak values can be obtained from tests over a wide range of concentrations using one chemical igniters (Crowl & Louvar, 1990). The explosion indices, Pmax and (dP/dt) max, are defined as the mean values of the maximum values of all three series. Subsequently, the gas or vapor deflagration index (Kg) is calculated from (dP/dt) max by means of the Cubic Law (NFPA, 1992)

$$V^{1/3}(dP/dt)_{max} = K_g$$

Where Kg and V are the maximum gas explosion constant specific to the gas and the volume of test apparatus. As there are many gas products and industrial practices, it is appropriate to assign this maximum constant to one of several explosion classes, and to use these as a basis for sizing explosive relief.

2.4.1 Minimum Oxygen Concentration (MOC)

The LEL is based on fuel in air. However, oxygen is the key ingredient, and MOC is required to propagate a flame. When oxygen concentration is less than the MOC, the reaction cannot generate enough energy to heat the entire gas mixtures (including the inerts) to the extent required for the self-propagation of the flame. MOC is an especially useful parameter, because explosions and fires are preventable by reducing the oxygen concentration regardless of the concentration of the fuel.

This concept is the basis for the common procedure called inerting. The MOC has units of percent oxygen in air plus fuel. If experimental data are not available, the MOC is estimated by using the stoichiometry from the combustion reaction and the LEL. This procedure works quite well for many hydrocarbons (Siwek, 1996; Crowl & Louvar, 1990).

2.5 Explosion Limits

The explosive limits of a gas or a vapour, is the limiting concentration (in air) that is needed for the gas to ignite and explode. There are two explosive limits for any gas or vapor, the lower explosive limit (LEL) and the upper explosive limit (UEL). At concentrations in air below the LEL there is not enough fuel to continue an explosion; at concentrations above the UEL the fuel has displaced so much air that there is not enough oxygen to begin a reaction.

Controlling gas and vapor concentrations outside the explosive limits is a major consideration in occupational safety. Methods used to control the concentration of a potentially explosive gas or vapor include use of sweep gas, an inert gas such as nitrogen or argon to dilute the explosive gas before coming in contact with air. Uses of scrubbers or adsorption resins to remove explosive gases before release are also common. Gases can also be maintained safely at concentrations above the UEL, although a breach in the storage container can lead to explosive conditions.

2.5.1 Lower Explosive Limit

Lower Explosive Limit (LEL): The explosive limits of a gas or a vapor are the limiting concentration (in air) that is needed for the gas to ignite and explode. The lowest concentration of a gas or a vapor in air capable of producing a flash of fire in presence of an ignition source (arch, flame, heat). At concentration in air below the LEL there is not fuel to continue an explosion.

Concentrations lower than LEL are "too lean" to burn. For example methane gas has a LEL of 4.4 % (at 138 ^{o}C) by volume, meaning 4.4 % of the total volume of the air consists of methane. At 20 ^{o}C the LEL is 5.1 %.

If the atmosphere has less that 5.1 % methane, an explosion cannot occur even if a source of ignition is present. When methane (CH_4) concentration reaches 5 % an explosion can occur if there is an ignition source. Each combustible gas has its own LEL concentration. These percentages should not be confused with LEL instrumentation readings. Instruments designed and calibrated to read LEL also read as percent values. (Jones, 1938; Crowl & Louvar, 1990).

2.5.2 Upper Explosive Limit

Upper Explosive Limit (UEL): Highest concentration (percentage) of a gas or a vapor in air capable of producing a flash of fire in presence of an ignition source (arch, flame, heat). Concentration higher than UEL are "too rich" to burn. Also called upper flammability limit (UFL).

2.5.3 Detonation

Detonation involves an exothermic front accelerating through a medium that eventually drives a shock front propagating directly in front of it. They are observed in both conventional solid and liquid explosives as well as in reactive gases. The velocity of detonations in solid and liquid explosives is much higher than that in gaseous ones, which allows far clearer resolution of the wave system in the latter.

Gaseous detonations normally occur in confined systems but are occasionally observed in large vapor clouds. Again, they are often associated with a gaseous mixture of fuel and oxidant of a composition, somewhat below conventional flammability limits.

There is an extraordinary variety of fuels that may be present as gases, as droplet fogs and as dust suspensions. Other materials, such as acetylene, ozone and hydrogen peroxide are detonable in the absence of oxygen; fuller lists are given by both. Oxidants include halogens, ozone, hydrogen peroxide and oxides of nitrogen and chlorine.

In terms of external damage, it is important to distinguish between detonations and deflagrations where the exothermic wave is subsonic and maximum pressures are at most a quarter [citation needed] of those generated by the former. Processes involved in the transition between deflagration and detonation are covered thoroughly by Nettleton.